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METAL BONDED ZIRCONIUM DIBORIDE

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FOREWORD

This report was prepared by George Don McTaggart, Tracy A. Willmore and Dwight G. Bennett at the University of Illinois in the Department of Ceramic Engineering. It summarizes work done on the development of metal bonded zirconium diborides.

The work was done under Air Force Contract No. W33(038) ac-14520 identified by Research and Development Order No. 506-67, Ceramic Components for Aircraft Power Plant, administered by the Power Plant Laboratory, Directorate of Laboratories, Wright Air Development Center, Mr. B. L. Paris acting as project engineer.

ABSTRACT

Zirconium diboride powders from two producers were combined with 20% by weight of either cobalt, chromium, nickel, or a mixture of cobalt plus chromium. Compacts and bars were formed using the techniques of powder metallurgy and fired in an argon atmosphere at temperatures exceeding the melting point of the metals. A discussion of the phases present before and after firing, as determined by X-ray techniques, is presented. Photomicrographs showing fired porosity and microstructure of the specimens are discussed. Modulus of rupture determinations and tests for oxidation resistance at 2000°F were made. The mixtures tested were found to have only moderate strength. Their oxidation resistance was too low for them to be considered for use at 2000°F in oxidizing atmospheres.

PUBLICATION REVIEW

The publication of this report does not constitute approval by the Air Force of the findings or the conclusions contained therein. It is published only for the exchange and stimulation of ideas.

FOR THE COMMANDER:

NORMAN C. APPOLD
Colonel, USAF
Chief, Power Plant Laboratory

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I. INTRODUCTION

The exacting requirements of the materials suitable for components of modern flight propulsion units have been set forth (Ref. 1, 2, and 3) in the literature many times. This investigation was actuated to study bodies composed of zirconium diboride bonded with various metals in order to determine whether or not the properties of such bodies would allow their being considered for use as materials for components of flight propulsion units.

II. DISCUSSION OF THE PROBLEM

1. Literature Review

Bodies of boron-bonded zirconium diboride have been reported (Ref. 4) to have outstanding high temperature strength, oxidation resistance and thermal shock resistance. Such bodies, however, were found (Ref. 5) to be unsuitable for use as gas turbine blades in jet engine application. Their brittleness and associated lack of impact strength proved to be the cause of failure.

One investigation (Ref. 6) revealed the formation of complex borides by the reaction of transition metals of the iron group with "zirconium boride" or with any boride of the metals of the IV, V, and VI group. In that investigation, attempts to bond zirconium diboride with metallic materials more ductile than boron were unsuccessful.

Bodies composed of zirconium diboride bonded with nickel and cobalt have been compounded (Ref. 6 and 7). While all of these bodies exhibited low modulus of rupture strengths and poor resistance to oxidation, the ones bonded with cobalt and formed into rocket nozzles were reported to perform outstandingly well.

2. Selection and Properties of Materials

Zirconium diboride was selected as the base ingredient for the experimental cermets because when hot pressed without additives, it was reported to have good high temperature strength, oxidation resistance and thermal shock resistance.

Considerable information is available on the system Zr-B as the result of the work of Glaser and Post (Ref. 8), Norton, Blumenthal and Sindeband (Ref. 9) and Kiessling (Ref. 10). Zirconium diboride is an interstitial compound having a simple hexagonal structure of the C32 type. The aforementioned authors are in very close agreement on the lattice constants and density of zirconium diboride. The lattice constants a_o and c_o are given as 3.170Å

and 3.533Å respectively. The ratio c/a is given as 1.11. The density of zirconium diboride is given as 6.09g/cc and its melting point as 3040°C.

Glaser and Post (Ref. 8) have proposed, and present evidence for, the existence of three compounds in the system Zr-B. These are zirconium diboride (ZrB_2), zirconium monoboride (ZrB), and zirconium dodecaboride (ZrB_{12}). Of these compounds, only ZrB_2 is reported to be stable in the presence of carbon. ZrB reacts with carbon to form ZrB_2 and ZrC (zirconium carbide), while ZrB_{12} reacts with carbon to form ZrB_2 plus a boron-carbide phase (Ref. 8).

Zirconium diboride has been found (Ref. 11) to be stable in the presence of nitrogen up to 1050°C.

Thermal analyses of zirconium diboride powders show (Ref. 12) a strong exothermic reaction at 625°C.

The selection of the bonding metals listed below was based on melting point, oxidation products, ductility, availability and on the results of previous investigations.

Metal	M.P. °F.	Density g/cc	Crystal Structure	
Co	2723	8.90	FCC	a_o 3.554Å
Ni	2650	8.90	FCC	a_o 3.5168Å
Cr	3270 ± 90	7.19	BCC	a_o 2.8796Å

Melting points and densities are from the Metals Handbook, American Society for Metals, (1948); Crystal structure data are from Wyckoff's Crystal Structures, Volume I, Interscience Publishers, New York, New York.

III. Experimental Procedure

All boride and metal powders used in this investigation were commercial products. Chemical analyses and particle size of the powders as received from the producers are listed in Table I.

In the initial phases of the study, Norton Co. zirconium diboride (ZrB_2) with an initial particle size of 40 microns and finer was further reduced by milling it for 50 hours in a tungsten carbide mill. Tungsten carbide balls were used as the grinding media and methanol as the mill liquid.

The slurry from the mill was transferred to a clean container and allowed to stand in air until the methanol had evaporated.

This produced a cake which was ground in an agate mortar to pass a 40 mesh screen. The resulting powder was then used as a standard source of milled Norton Co. ZrB_2.

The milling operation required close supervision since there appeared to be a reaction between the methanol and the ZrB_2. Such high pressures were produced that it was necessary to vent the mill periodically in order to prevent its end plates from being dislodged. The end product was assumed to be either trimethylborine $(CH_3)_3B$ (Ref. 13) or methyl borate $(CH_3)_3B_2O_3$ (Ref. 14). In spite of this evidence of reaction no undesirable effect on the ZrB_2 could be detected.

In view of the apparent reaction noted, benzene was tried as a mill liquid. It seemed to be quite inert to the ZrB_2 but the fired body produced from the milled material was considerably less resistant to oxidation than those prepared with methanol. The use of methanol was therefore continued.

The first experimental bodies (D-1 through D-7) were prepared by combining the proper amounts of the minus 40 mesh diboride and minus 300 mesh cobalt metal powders in an agate mortar, adding benzene to facilitate mixing and then mixing-grinding until the benzene had evaporated. The dry mixture was passed through a 40 mesh screen. Cylindrical specimens one-half inch in diameter and approximately three-eighths inch high were then made by dry pressing in a hardened steel mold to 50,000 psi.

The compositions of all bodies and pertinent data with regard to their batch mixing are given in Table II.

The cylindrical specimens were fired in dried, oxygen-free argon in a tungsten resistance furnace. The heating element is in the form of a helical coil constructed to surround the specimen. A photograph of the furnace assembly is shown in Figure 1.

The specimens were brought up to the maximum firing temperature shown in Table III, in about one-half hour, held at temperature for one-half hour and then allowed to cool with the furnace.

Each fired cylinder was cut in half with a diamond saw. One half was retained to be mounted for microscopic examination, if such was warranted, and the other was crushed and ground to pass a 200 mesh screen. Powders so prepared were then x-rayed with a Norelco Geiger Counter X-ray Spectrometer equipped with an iron tube. The resulting x-ray patterns were analyzed to determine if reactions had occurred between constituents or if any other signs of thermal alteration could be detected. Identification of the phases present was made by comparison of the interplanar ("d") spacings with those recorded in the ASTM index or by comparison with patterns made of the separate constituents prior to firing.

In the initial test, body No. D-1 composed of 80 weight per cent of Norton Co. ZrB_2 and 20 per cent of cobalt was investigated. When it was fired in argon at temperatures up to 3200°F a hard strong body with only moderate shrinkage, expressed as per cent of the unfired dimension, resulted. The evident tendency of the body D-1 to develop a sound fired structure was encouraging but x-ray studies introduced some complications. The patterns showed the presence of zirconium carbide and some unidentified phases which might have been due to alteration of the bonding metal.

In attempting to properly interpret such results certain known factors were considered. The ZrB_2 used (cf Table I) contains about 0.5 per cent of free carbon. After synthesis, the ZrB_2 was reduced in size by the manufacturer to 325 mesh by grinding it in mills employing boron carbide balls. The presence of B_4C in the "as received" material was apparently substantiated by a peak in the x-ray pattern which corresponded to the principal line of B_4C. Both B_4C and carbon are undesirable in diboride-base cermets because the binder metals would react with any B_4C and to a lesser extent with carbon to form metal borides and carbides.

Attempts were made to eliminate B_4C and free carbon from the Norton Co. ZrB_2 by additions of either 5 or 10 per cent of zirconium metal powder. It was thought that the Zr might react with any B_4C or carbon in the mixture to form ZrB_2 and ZrC. Such batches, with Zr additions, were pressed into compacts which were fired at 3400°F in argon. This "pre-reacted" material was crushed and ground to minus 325 mesh. The powder was mixed with 20 per cent by weight of minus 300 mesh cobalt and cylinders pressed from the resulting mixture. When fired at 3400°F these specimens were weak and porous. Their x-ray patterns showed appreciable quantities of zirconia (ZrO_2) to be present. The peak corresponding to 2.38Å also persisted which was a strong indication that it was not due to B_4C as was initially thought to be possible. Zirconium hydride (ZrH_2) was substituted for Zr in body D-7b in an attempt to remove any oxygen present during firing but no improvement in the fired bodies could be noted.

Since attempts to improve Norton Co. ZrB_2 with zirconium were unsuccessful, some means of purification were sought. Since iron was known to be present, the milled ZrB_2 was leached with 10% acetic acid and then washed with distilled water and methanol to remove it, and, it was hoped, any other metallic contaminants.

Cylinders prepared from body D-7 (80% processed ZrB_2 and 20% Co) were fired at temperatures comparable to those used for body D-1 in which unleached ZrB_2 was used. Some improvement in both fired structure and density was noted.

All mixing of metal powders and ZrB_2 had been done by hand up to this time. To investigate the affects of more intimate

mixing, the components of body D-7a (80% acid leached ZrB_2-20% Co) were milled together for 20 hours in methanol in the tungsten carbide mill. Fired specimens of this body showed appreciable improvement in structure when compared to body D-7. Although the powders must have been reduced somewhat in particle size during the additional milling time, the improvements noted were believed to be largely due to the more intimate mixing obtained. Since 20 hours of mixing by ball milling was found to be definitely beneficial, it was later practiced in the fabrication of bars to be used for physical property determinations.

In view of the results described above, Norton Co. ZrB_2 was used in additional bodies containing either nickel or chromium as the binder metal (Bodies D-9a and D-11 respectively). The ZrB_2 which had been reduced in particle size by 50 hours of milling in methanol and then acid leached was intimately mixed with the selected binder metal by 20 hours of milling. The bodies so prepared and then fired were found to have good sound structures. This work plus that done on cobalt bearing bodies established the proper techniques to use with Norton Co. ZrB_2 and also the approximate firing ranges of the various metal - ZrB_2 combinations.

Because of the relatively low purity of Norton Co. ZrB_2, a sample of "high purity" ZrB_2 had been obtained from the American Electro Metals Corporation, Yonkers, New York. Experimentation with this material was begun at this time.

The information obtained from the foregoing experiments concerning fabricating and firing techniques made it feasible to convert from a cylindrical to a bar type specimen from which more useful information could be obtained. Body preparation and forming techniques were also standardized.

Norton Co. ZrB_2 was prepared by subjecting the "as received" material to a 50 hour grind in methanol in the tungsten carbide mill. The dried, milled powder was leached with 10% acetic acid and then subjected to two washings, first with distilled water and then with methanol. The American Electro Metal ZrB_2 was neither subjected to the 50 hour grind nor the acid leaching since it had a nominal average particle size of 2-4 microns and was reported to be quite pure as received.

Body mixtures containing ZrB_2 from either of the vendors noted were proportioned by weight and mixed by 20 hours of milling in methanol in the tungsten carbide mill. The resulting slurries were dried in air and then granulated through a 40 mesh screen. To facilitate the forming of the bars, five per cent by weight of Carbowax 4000 was added as a lubricant. The wax was dissolved in hot benzene and the solution added to the dry body. The mixture was stirred in an agate mortar until the benzene had evaporated. It was then granulated through a 40 mesh screen

The granulated material was pressed at 30,000 psi to a

thickness of about 0.25 inch in a hardened steel mold with inside dimensions of 2.96 in. by 0.40 in. Since considerable difficulty was experienced with pressure cracks in the pressed bars, a change was made to hydrostatic pressing. This eliminated pressure cracking. In hydrostatic pressing, the bars were "preformed" by pressing the powders at 5000 psi. They were then encased in thin-walled rubber cylinders and subjected to a pressure of 40,000 psi in a hydrostatic pressing chamber containing glycerine.

Adequate dewaxing was accomplished in a circulating atmosphere of argon in a small electric furnace that was specially constructed for such purposes. The furnace was slowly brought up to a maximum temperature of 575°F and held there for about two hours.

Each dewaxed bar was cut in half with a hack saw to form two bars about 1 3/8 inches in length. These bars were fired in the tungsten resistance furnace shown in Figure 2. The heating element consists of 32 tungsten rods 0.065 inch in diameter and 14 inches long, hanging vertically and so arranged as to enclose a heating chamber 2 in x 3.5 in x 12.5 in deep.

One half of the rods are suspended from each of two water cooled copper electrodes. These two groups of rods are connected at the bottom by a molybdenum "shorting" ring to form a parallel-series circuit. The element, assembled as described, is enclosed within two concentric, cylindrical molybdenum disks. Power is supplied to the furnace through a bank of three transformers rated at 30 KW at 20.5 volts which can be connected in several ways through a series of switches to give five coarse voltage control steps. Fine control in each step is obtained with a 220 volt variac transformer. The primary voltage to the transformers is 220 volts and by the means described above the secondary voltage can be varied continuously from 0.0 to 20.5 volts.

The specimens, during firing, were located in the center of the chamber on a graphite block suspended by four graphite rods. Zirconium diboride (ZrB_2) and zirconia (ZrO_2) powders were used to separate the bars from the graphite block. Zirconia was the more satisfactory as the binder metals in the cermets would wet the powdered ZrB_2 and cause it to stick to the bars. The temperature was measured by sighting an optical pyrometer on the specimen through a glass prism located on top of the furnace shell. No corrections were made for absorption by the prism or for variations in emissivity.

A mechanical pump was used to evacuate the furnace chamber to a pressure of 100 microns of mercury or less. Dried, oxygen-free argon was then introduced into the furnace until the pressure in the chamber slightly exceeded eight cm of mercury above atmospheric pressure. At this pressure the argon circulated through

the system and escaped through a column of mercury. After flushing the system for about five minutes, the argon was cut off and the furnace evacuated again. Argon was then readmitted to the furnace and allowed to circulate for the first five minutes of the firing cycle. Thereafter the argon was cut off and firing proceeded in a static argon atmosphere at a pressure of eight cm of mercury above atmospheric pressure.

Initially, a firing schedule of two hours was used. In this case the heating was too rapid and some of the specimens cracked badly. When the time taken to reach maximum temperature was increased to five and six hours, sound bars were obtained. With the slower rate of heating, the specimens were at a temperature well above the melting point of the bonding metal phase for a considerable period of time and at the final temperature for from two to three minutes. The specimens were then allowed to cool with the furnace.

The faces of the fired bars were ground flat on a diamond grinding wheel to prepare them for modulus of rupture determinations. The apparatus initially used for modulus of rupture tests was designed in the Department of Theoretical and Applied Mechanics at the University of Illinois. It is shown in Figure 3. Compensation for warpage in the bar or for non-parallelism of the faces was made by movements of the knife edges. The advantages of this apparatus were offset by the difficulty of its adjustment and the time-consuming nature of the operation. A second device for modulus of rupture testing (Figure 4) was therefore constructed which had fewer adjustments but at the same time had sufficient flexibility to compensate for minor inaccuracies. Both devices were mounted in a lever loading type Tinius Olsen machine. The breaking span was 1.0 inches for both. It was possible to apply load either by a hand crank or a variable speed electric motor but the hand crank was used since the slowest possible rate of mechanical loading seemed to be too rapid. With the hand crank, however, some variation in loading was unavoidable.

One half of each bar broken in cross bending was used to determine bulk density by the suspended weight method. Values reported are therefore the averages of several determinations. Zylene (sp gr 0.8641) was used as the saturating and suspending medium. Saturation was accomplished by exposing a container in which the specimens were immersed to a partial vacuum. An analytical balance was used to make all weighings.

One half-bar of each body was mounted in lucite for microscopic study of the structure in the as-fired condition. A second half-bar was crushed and ground to pass a 200 mesh screen and the powder x-rayed to check the results previously obtained with cylindrical specimens.

Other halves of modulus of rupture test bars were used to make a comparative test of the resistance of these bars to

oxidation. The specimens were placed on an Inconel plate and exposed at 2000°F to the normal atmosphere of a small electric furnace. Separate sets of specimens were oxidized at 5, 10, 15, 20, and 60 hours. The effects of the oxidation treatments were determined by visual inspections, x-ray diffraction and microscopic examination of the bodies.

Each oxidized specimen was sawed into two parts with a diamond cut off wheel. One half was crushed in a hardened steel mortar to pass a 200 mesh screen. The powders were x-rayed with the Norelco unit and the resulting patterns analyzed to determine the products of oxidation. The cut face of the other half was ground flat on a diamond grinding wheel and the specimen mounted in lucite in preparation for polishing.

The polishing of all fired specimens, either oxidized or unoxidized, was a difficult, time consuming task. Felt lap wheels impregnated with coarse and then fine diamond dust were first used. The felt lap was kept saturated with methanol to provided adequate lubrication. Some difficulty was experienced in this respect since if the felt was allowed to get too dry, both specimen and lucite mounting would get hot. Cracked and unsatisfactory mounts were the result. Using extreme care, however, polished sections could be obtained with this technique.

The technique which was adopted involved a rough grind on either a lap covered with 240 grit silicon carbide paper and wetted with water or on a glass plate covered with 600 mesh boron carbide suspended in oil. The specimens were then transferred to a felt covered lap wheel impregnated with a medium fine diamond finishing compound suspended in spindle oil. A second felt covered lap wheel impregnated with extra fine diamond finishing compound in kerosene was then used. Rouge, on a felt covered wheel, was used for a brief final polishing to emphasize the details of the internal structure of the body.

IV. RESULTS AND DISCUSSION

1. X-ray Analyses

When the ZrB_2 from the two different sources was x-rayed in the "as received" condition, two interplanar spacings were obtained in each case which were not listed in the "d"-spacings adopted as standard for this investigation.* These spacings were equal to 3.04Å and 2.39Å and corresponded to peaks on the Norelco patterns (Figure 5) at 37.3° and 47.8°, respectively. These peaks persisted in the x-ray patterns of all subsequent experimental bodies. The bodies were quite diverse in composition and in many instances contained ingredients that would have reacted with any logical contaminants to which these extra peaks could be attributed. It was

* Since no standard interplanar spacings for ZrB_2 are recorded in the ASTM Index, the values adopted for this compound were obtained from the Norton Company.

therefore concluded that they were characteristic of the particular stocks of ZrB_2 used. They were so considered in the analyses of all x-ray results.

Processing Norton Co. ZrB_2 by ball milling, acetic acid leaching, and washing with water and then methanol caused a minor change in the x-ray pattern (Figure 5). An additional peak appeared at 45.0° (2.53Å) which was probably due to tungsten carbide (WC) picked up from the mill and balls during grinding. Firing this processed material without additives resulted in further changes as can be seen in Figure 5. The peak at 45.0° disappeared but additional peaks appeared at 50.2° (2.28Å), 54.9° (2.10Å) and 43.4° (2.61Å). The peak at 50.2° probably was due to alpha W_2C which was formed from the WC. The latter two peaks did not occur in the patterns when ZrB_2 from either company was fired "as received" which shows that they were not due to thermal alteration of some constituent in the original material. The same two peaks were also present in most of the patterns subsequently obtained for fired metal-ZrB_2 combinations, regardless of the source of the ZrB_2 or the metal added. These peaks usually appeared in the same pattern but in isolated cases the peak for the 2.61Å line occurred without that for the 2.10Å line. Such results indicate the formation of a definite structure - directly due to processing and firing - in those bodies which contained milled ZrB_2. The material responsible for the two extraneous lines could not be identified. It is probable, as will be explained later, that they are due to a zirconium-base material.

The possibility that these peaks might be due to a zirconium-boron-oxygen compound, formed during firing from residues from the action of the methanol on the ZrB_2, was discounted when attempts to produce such a compound by heating different combinations of zirconium and boric oxide in air did not produce a material whose x-ray pattern had matching peaks.

More complex results were obtained when the fired bodies of the cobalt series were x-rayed. Comparison of the patterns in Figure 6, which are typical of this group, with those in Figure 5 shows that several new peaks appeared.

Study of all the patterns for this group disclosed that ZrO_2, as well as the material responsible for the two lines 2.61 and 2.10Å, was present in all the bodies to which only cobalt had been added. Almost every x-ray pattern also had a moderately strong peak corresponding to a "d"-spacing of 1.99Å. One exception was that of body D-12 which contained 80% AFMC ZrB_2.

The indications of the presence of elemental cobalt in those bodies were inconsistent, although 20, 25, and, in one special case, 30% was added. Similar results were noted in an investigation of cobalt bonded TiC in which cobalt could not be detected in amounts up to 30% (Ref. 16). Wyckoff (Ref. 17) mentions that cobalt may be altered by grinding so that mixed packing of cubic

and hexagonal modifications results. In this case many of the x-ray reflections become diffuse. Similar conditions may have been encountered in this investigation.

In addition, in the patterns of the cobalt series, peaks which were generally very small and which corresponded to "d"-spacings of 2.69, 2.33, 1.66 and 1.46 Angstroms appeared for the first times. However, not every one of these appeared in every pattern and none of them appeared in the pattern of body D-12. These may indicate the presence of ZrC but this identification is made with reservations in view of the possibility that the lines may be due to a solid solution of ZrC and ZrB. It is theorized that these peaks did not appear in the pattern of body D-12 because the firing temperature, 2830°F, of this body was below that necessary for solution. Some support is given to this theory from the patterns for all bodies which contained binder metals. It was noted that the relative intensities of the peaks under discussion increased directly with firing temperature.

The possibilities for the formation of a solid solution of ZrC-ZrB are based on the following factors. While these are presented during the discussion of the bodies of the cobalt series, the same considerations apply to all metal bonded bodies.

The monoboride of zirconium, which was reported to have an x-ray pattern identical to that of ZrC, has been proposed (Ref. 8). ZrB is considered unstable at room temperature in the presence of 0.5% or more of carbon, reverting to ZrB_2 and ZrC (Ref. 8). However, it has been reported that the temperature dependence of the cubic monoborides can be 'eliminated' through small percentages of the parent carbide in solid solution. With about 15% by weight ZrC in solution with ZrB, its temperature range can be extended to the melting point" (Ref. 15).

In this investigation, the height of some of the peaks - which is an indication of the amount of the phase present - attributed to ZrC are such that it is difficult to account for enough carbon contamination to produce so much of the compound. But if ZrB was formed by a reduction of the boron content through the action of the methanol, the proposed ZrC-ZrB solid solution could easily be present in amounts sufficient to produce the sizes of peaks encountered. Therefore, although the "d"-spacings under discussion are referred to in this report as identifying ZrC, it should be kept in mind that this phase may be a solid solution which includes ZrB and ZrC.

A special body was prepared to demonstrate that the lines 2.69, 2.61, 2.33, 2.10, 1.66 and 1.46 Angstroms could conclusively be associated with zirconium compounds. This was composed of 20% Co-4% B_4C-76% Norton Co. processed ZrB_2 and it was fired at 2950°F.

The addition of 4% B_4C to the Co-ZrB_2 combination was expected to provide an excess of boron so that any possible deficiency of this element in the processed ZrB_2 would be alleviated. Since it

was known that ZrB_2 is more stable than either ZrB or ZrC, these were not expected to be present after the body had been fired. The boron from the B_4C would react with the ZrC and ZrB to form ZrB_2. Any boron in excess of the requirements for these conversions would react with the cobalt.

The x-ray pattern of this body (Figure 6) showed that the only zirconium compounds present were ZrB_2 and ZrO_2. There was some evidence that the carbon had combined with the cobalt to form cobalt carbide (Co_3C) and strong evidence that cobalt monoboride (CoB) had formed.

The patterns (Figure 7) of bodies D-9a and D-13, which contained Ni and Norton or AEMC ZrB_2, respectively, showed that elemental Ni, ZrB_2, ZrO_2 and "ZrC" were present after firing. The 2.10Å line was present in the pattern of body D-13 (AEMC ZrB_2) but not in that of body D-9a. Moderately strong peaks equivalent to "d"-spacings of 1,92Å and 1.62Å were also obtained for body D-13. Neither of these was identified with any specific compound.

Analysis of the x-ray patterns (Figure 8) of the two chromium bonded bodies revealed the presence of Cr, ZrB_2, ZrO_2 and "ZrC". It was noted that elemental chromium was much more strongly indicated in body D-11 than in D-14 and also that body D-14 produced a line at 2.10Å while body D-11 had one at 1.99Å. No logical explanation for this erratic behavior has been developed.

The x-ray pattern of body D-18 (Figure 9) which contained 10% Co-10% Cr - 80% AEMC ZrB_2 showed that the two metals formed a solid solution as was desired. This fired body also contained ZrO_2, "ZrC" and the same unidentified phases which had been encountered in other bodies.

2. Microscopic Examination

Photomicrographs of all compositions at 100X, as shown in Figures 10 through 17, were made to compare their porosities. The photomicrographs are somewhat misleading since an unidentified solid phase cannot readily be differentiated from the actual voids. This condition is exemplified by cobalt bonded body D-12 which shows (Figure 13) a large number of dark areas and, apparently, a high porosity. Examination of the same body at 1000X (Figure 21) showed that most of the black areas were a solid phase of glass-like texture and color. Chromium bonded bodies contained the least amounts of this unidentified phase. For example, the dark areas shown in Figure 12 (chromium bonded ZrB_2) are voids while those in Figure 13 (cobalt bonded ZrB_2) are a mixture of voids and the unidentified phase.

Body D-11, chromium bonded ZrB_2, had an unusual fired structure which may be seen in Figure 12. Within the body were small granules separated from the matrix. They were the result of incomplete breaking up of the cake of the freshly ground body mixture during

the granulating process. This left small, hard nodules composed of particles in very intimate contact by virtue of the settling action of the solids during the evaporation of the methanol. Forming pressures were not high enough to crush them and the loose powder surrounding them was not compacted to an equivalent density. When fired there was a differential shrinkage sufficient to separate the nodules from the matrix. The internal cracks so introduced had a detrimental effect on the modulus of rupture as may be seen from the results summarized in Table III.

Microscopic examination of all of the bodies at 1000X revealed several general characteristics. The structure of all bodies consisted of a continuous ZrB_2 skeleton filled in with the binder metal. There appeared to be very little difference in the structure of the ZrB_2 from the two different sources.

Growth of the ZrB_2 grains was evident in every case. As can be seen from the photomicrographs in Figures 18 through 25, the structures of the skeletons and of the individual grains varied depending upon the metal used. Cobalt promoted the formation of large, well rounded grains. When nickel was used, the ZrB_2 grains were smaller and possibly slightly more angular. With chromium, the grain size of the diboride was similar to that in the nickel bodies but the grains were more angular and tacked together at edges and ends to form the skeleton. Also, the skeleton appeared to be more continuous. The most prominent example of grain growth occurred in the cobalt-chromium bonded body D-18 (Figure 25).

It is possible that grain growth was affected by the degree of fluidity of the metal during the maturing fire. The firing temperatures used approached the melting point of chromium but were 200°F or more above the melting point of cobalt.

An unidentified phase, dark brown to black in color and with a vitreous luster, was present to some extent in every body. Some grains were semi-transparent. When observed in its various forms, the term "glass-like" seemed to aptly describe this phase. It was not affected by long immersion in hot water and the $HF-HNO_3-CH_3OH$ etching solution attacked it only to about the same degree as it did the ZrB_2. Though visually strongly resembling a glass, some hesitancy was felt in positively identifying it as such since the formation of a highly stable glass from materials available in the experimental compositions seemed unlikely. This phase appeared in the largest amounts in cobalt bonded bodies and to the least extent in chromium bonded bodies.

The photomicrographs of the etched specimens show a rather interesting characteristic of the ZrB_2 itself. Many of the grains show raised portions which might be described as plateaus. Since careful inspection of individual grains in the unetched state had not revealed any evidence of discontinuities corresponding to these plateaus, it was concluded that this condition is due to preferential etching.

The microscopic studies did not effectively differentiate between the various phases which the x-ray analyses indicated were present. Cobalt was revealed whereas in the x-ray analyses there was no very strong indication of its presence. Solution effects were evident in the cobalt and cobalt-chromium bonded bodies through the growth and rounding of the grains. The ZrO_2, not found in microscopic studies, was probably due to oxygen adsorbed during milling and was therefore well dispersed. The clusters of a gray material noted in many bodies might possibly be the "ZrC" phase shown in x-ray patterns.

3. Physical Properties and Sintering Characteristics

The physical properties determined for the ZrB_2 base cermets are given in Table III. The procedures used in body preparation are given in Table II.

Data for the cobalt bonded series (Bodies D-1 through D-7b) show the beneficial effects derived from acid leaching and mechanical mixing of bodies containing Norton Co. ZrB_2. The addition of zirconium, either as the element or as ZrH_2, did not improve the sintering characteristics of cobalt bonded compositions.

The densities of the different metal bonded bodies except those bonded with chromium did not closely approach the theoretical densities for such compositions. Bodies containing Norton Co. ZrB_2 had, except in the case where chromium was added, consistently higher densities than their AEMC ZrB_2 counterparts.

The substitution of 10 per cent chromium for cobalt in Body D-18 did not produce any change in physical properties from those of the comparable cobalt body. This substitution, however, was made in an attempt to increase the oxidation resistance rather than to produce any decided change in other physical properties. Simultaneously reducing the cobalt content and increasing the firing temperature of the Co-AEMC ZrB_2 series (Body D-17) likewise did not effect much change.

The x-ray analyses showed, in all cases, the presence of considerable extraneous material.

In general, all bodies were quite porous. Body properties could probably be improved by changes in processing techniques provided the reasons for the alteration of constituents during firing were clearly understood.

The modulus of rupture values listed in Table III are quite low when compared to values reported for some of the more highly developed TiC base cermets. However, due to lack of standardization in specimen size and breaking span, the results are not necessarily directly comparable.

Of all bodies tested, those bonded with chromium were the strongest. The nodular nature of body D-11 (Figure 12) as compared to body D-14 (Figure 15) explains the difference in strength

of the two bodies. The nodular structure of body D-11 with voids around the nodules and the reasons for this condition have already been discussed. Both bodies were fired to 3275°F, the limit of the furnace. An increase in the firing temperature to about 3400°F would probably produce an increase in strength through a better bonded body.

There appears to be a relationship between the strength of the various bodies and the amount of "glass-like" phase present. Those with the greatest amount of this phase had the lowest strength.

4. Oxidation Tests

The results of the comparative oxidation tests are shown in Figures 26, 27 and 28 and in the x-ray patterns shown in Figures 6, 7, 8 and 9.

The compositions containing cobalt, nickel, and cobalt plus chromium oxidized badly during 60 hours of heating at 2000°F in still air. The chromium bonded bodies were more resistant to oxidation but in all cases the reaction was so great that weight change data were not taken.

A glass of high B_2O_3 content was quickly formed on the surface of the cobalt bonded specimens. As oxidation progressed, the glassy phase seemed to be concentrated at the oxidized-unoxidized interface as it moved progressively into the body. This left a porous surface layer composed principally of ZrO_2 but containing some $CoO \cdot Co_2O_3$.

The nickel bonded bodies had reacted severely after 5 hours heating. The porous nature of the bodies may have permitted rapid penetration of oxygen. X-ray patterns of the oxidized surfaces did not, in general, contain peaks for the original constituents or of any of the anticipated products of oxidation. Body D-9a, however, was found (Figure 7) to contain appreciable amounts of ZrO_2 after the 60 hours of heating in air at 2000°F.

The reaction products constituted weak, porous layers which could be separated with ease from the specimens.

Visual examination of the specimens bonded with the cobalt-chromium combination was misleading since there appeared to only slight surface oxidation. Sectioning of the specimens, however, revealed deep penetration. The x-ray analysis showed a breakdown of the Co·Cr solid solution with chromium being detected but not cobalt.

The chromium bodies, as was noted, were the most resistant to oxidation. It is probable that a surface layer composed of the oxides of chromium, zirconium and boron was formed in such proportions that it did not become fluid at 2000°F but fused sufficiently

to form a protective barrier.

In all cases, the principal oxidation product was ZrO_2. The large quantities present are indicative of the poor oxidation resistance of ZrB_2. Only chromium showed an indication of producing sintered bodies which had appreciable oxidation resistance at 2000°F.

V. SUMMARY

When zirconium diboride was milled in methanol, a reaction occurred which yielded a product having a very high vapor pressure. The product of this reaction may be either trimethylborine or methyl borate. X-ray patterns of such ZrB_2 samples fired without metal additives indicated that a new but unidentified phase had been developed. This could possibly have been a zirconium compound. No detrimental effects could be directly attributed to the reaction or to the new phase developed.

Benzene, when substituted for methanol as the mill fluid, did not appear to react with the ZrB_2 but resulting bodies had poorer oxidation resistance than those containing ZrB_2 milled in methanol. Leaching Norton Co. ZrB_2 in acetic acid to remove iron produced beneficial results when the leached material was used in metal-ZrB_2 bodies.

Zirconium diboride was bonded by additions of 20 per cent by weight of cobalt, nickel, and chromium, or a mixture of ten per cent cobalt and ten per cent chromium by firing in an argon atmosphere at temperatures equal to or above the melting points of the respective metals. All bodies consisted of a continuous ZrB_2 skeleton filled in with the bonding metal. In all cases the ZrB_2 underwent considerable grain growth. The cobalt bearing bodies developed the largest grains. The degree of grain growth appeared to be affected by the fluidity of the metals present. Bodies fired at or near the melting point of the binder metal exhibited sintering with but little grain growth whereas bodies fired at temperatures appreciably above the melting point of the binder metals showed considerable grain growth.

No particular advantage was found in using high purity ZrB_2 nor were any radical structural differences noted for comparable bodies containing ZrB_2 from the two sources.

The zirconium diboride cermets developed a phase during firing which was conditionally identified as ZrC on the basis of the x-ray analyses. Data showing that this phase may have been a solid solution of ZrC and ZrB were presented. Some inconsistencies in the x-ray results were noted; in isolated cases, "d"-spacings could not positively be assigned to specific compounds.

Many of the fired compositions contained an unidentified "glass-like" phase. The amount of this material varied with composition, and it was most prevalent, as determined optically, in

bodies containing cobalt. Some correlation between the amount of this phase and the modulus of rupture seemed to exist.

No evidence of the borides of the bonding metals was found by x-ray analyses of the fired metal - ZrB_2 combinations. When B_4C was deliberately added, borides of the bonding metal were easily detected.

Cobalt was shown by microscopic techniques to be present in Co-ZrB_2 bodies. The weak indication of Co by x-rays may be explained by Wyckoff's mixed packing theory. Chromium and nickel were found by both techniques.

The bodies tested had only moderate transverse strength. The physical properties of the bodies could probably be improved by changes in processing techniques which would be contingent upon an understanding of the reason for the appearance of new phases and their subsequent elimination.

The resistance to oxidation was too low for these bodies to be seriously considered for use at 2000°F in oxidizing atmospheres.

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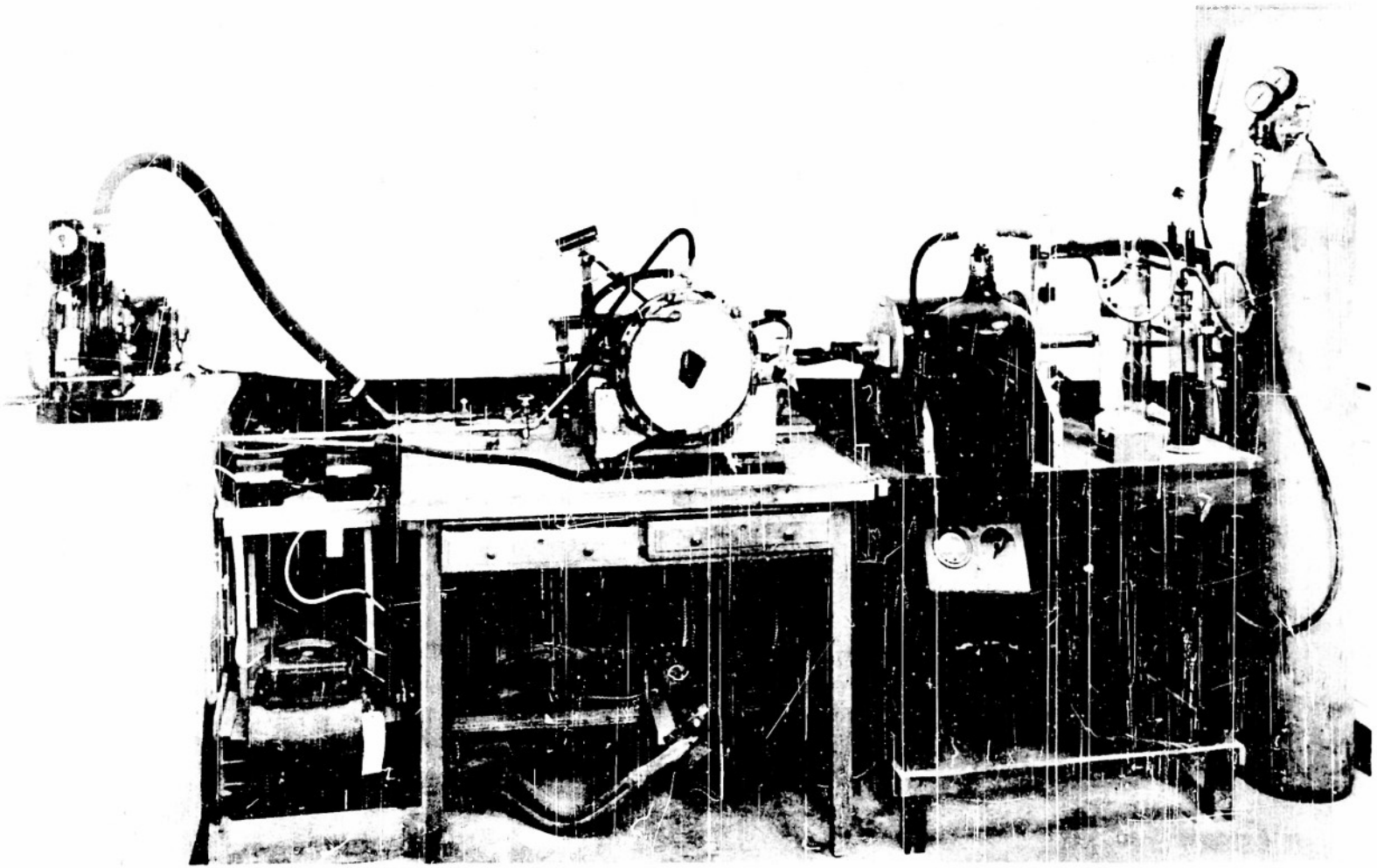


Figure 1. - Tungsten Coil Resistance Furnace and Auxiliary Equipment

a. Furnace chamber
b. Tungsten coil
c. Water cooled shell
d. Water cooled electrodes
e. Transformer
f. Variac
g. Tilting McLeod gauge
h. Gas outlet
i. Mechanical vacuum pump
j. "Drierite"
k. Pyrogallal + NaOH
l. Argon supply

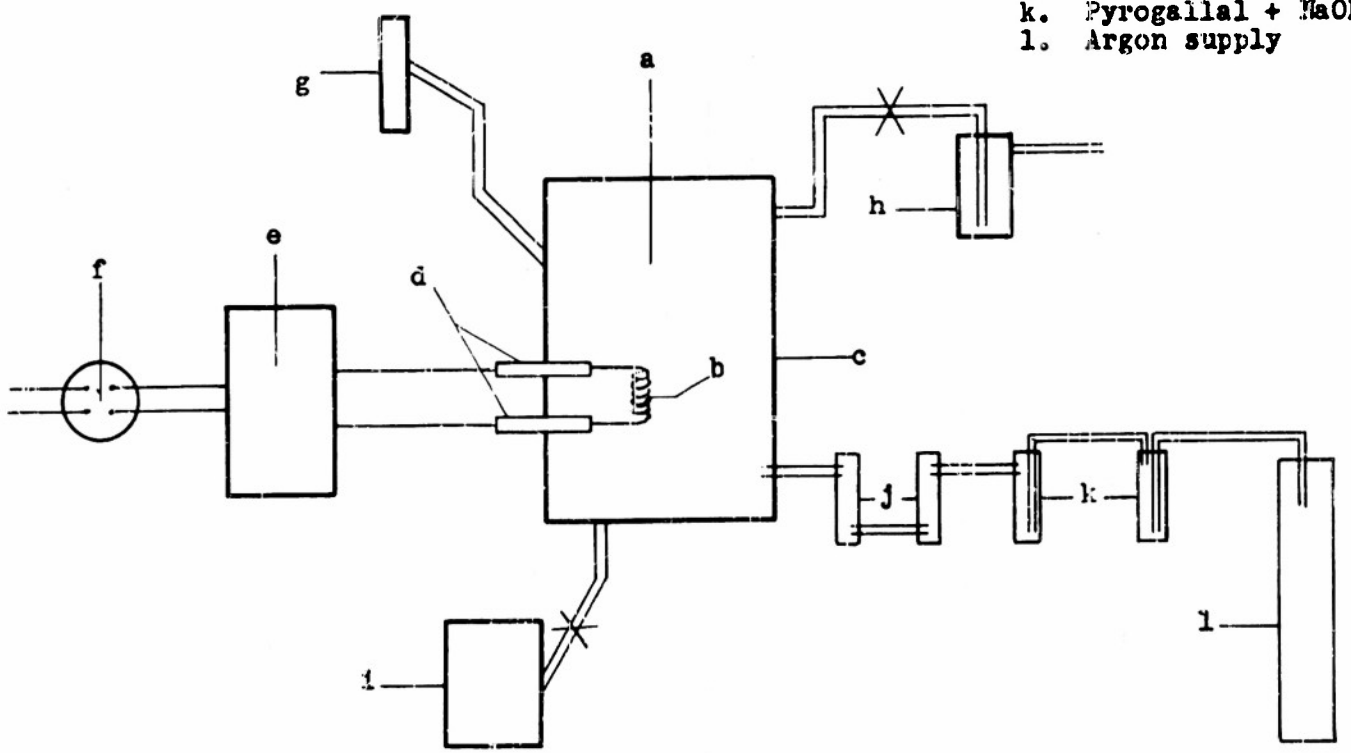


Figure 1a. - Schematic Diagram of Tungsten Coil Resistance Furnace and Auxiliary Equipment

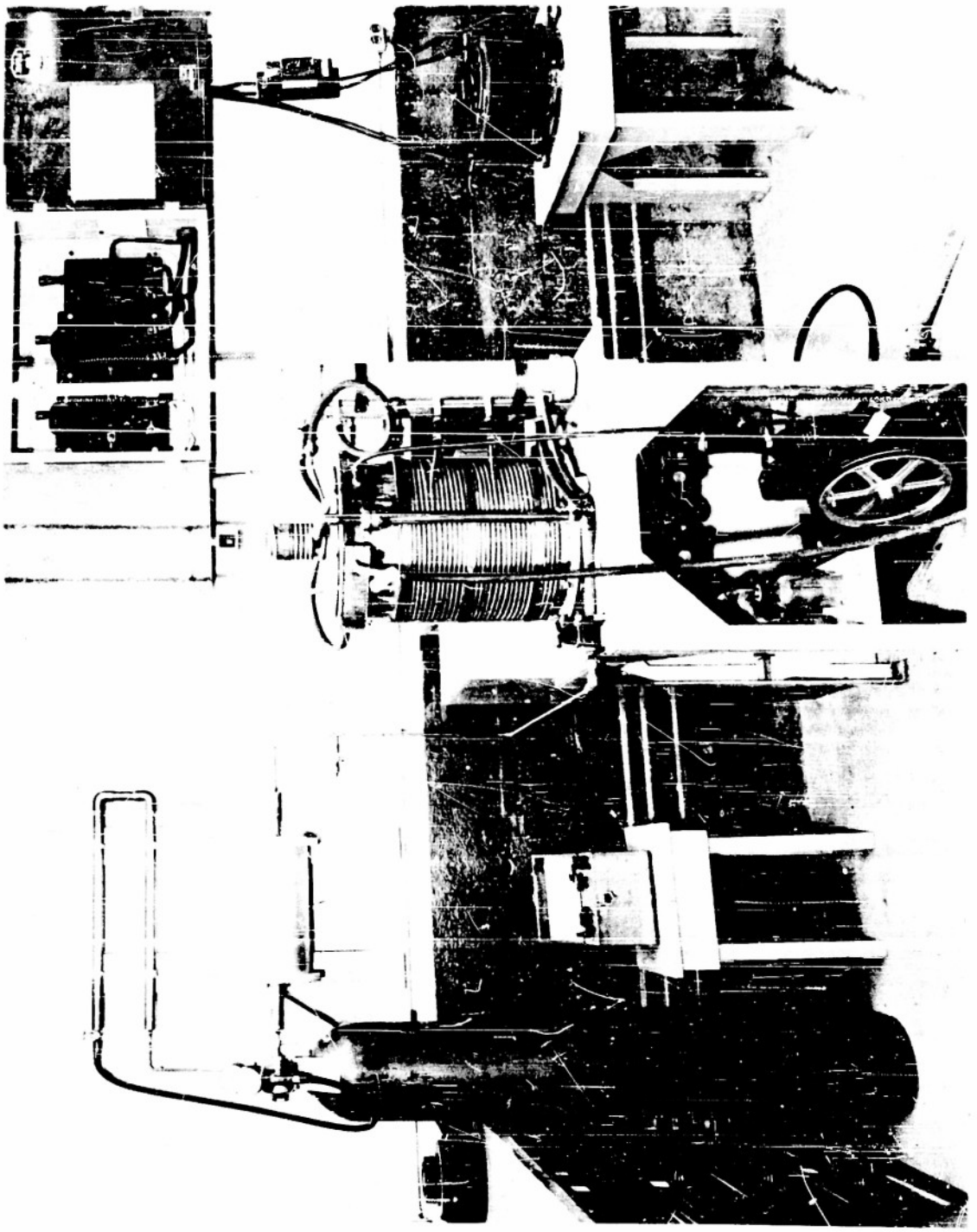


Figure 2. - Tungsten Grid Resistance Furnace and Auxiliary Equipment

a. Argon tank
b. Heated sponge zirconium
c. Sighting prism
d. Water cooled shell
e. Radiation shields
f. Tungsten elements
g. Copper electrode
h. Tilting type McLeod gauge
i. Mercury trap
j. Vacuum pump
k. Transformer
l. Circuit selector switches
m. Variac
n. Main switch

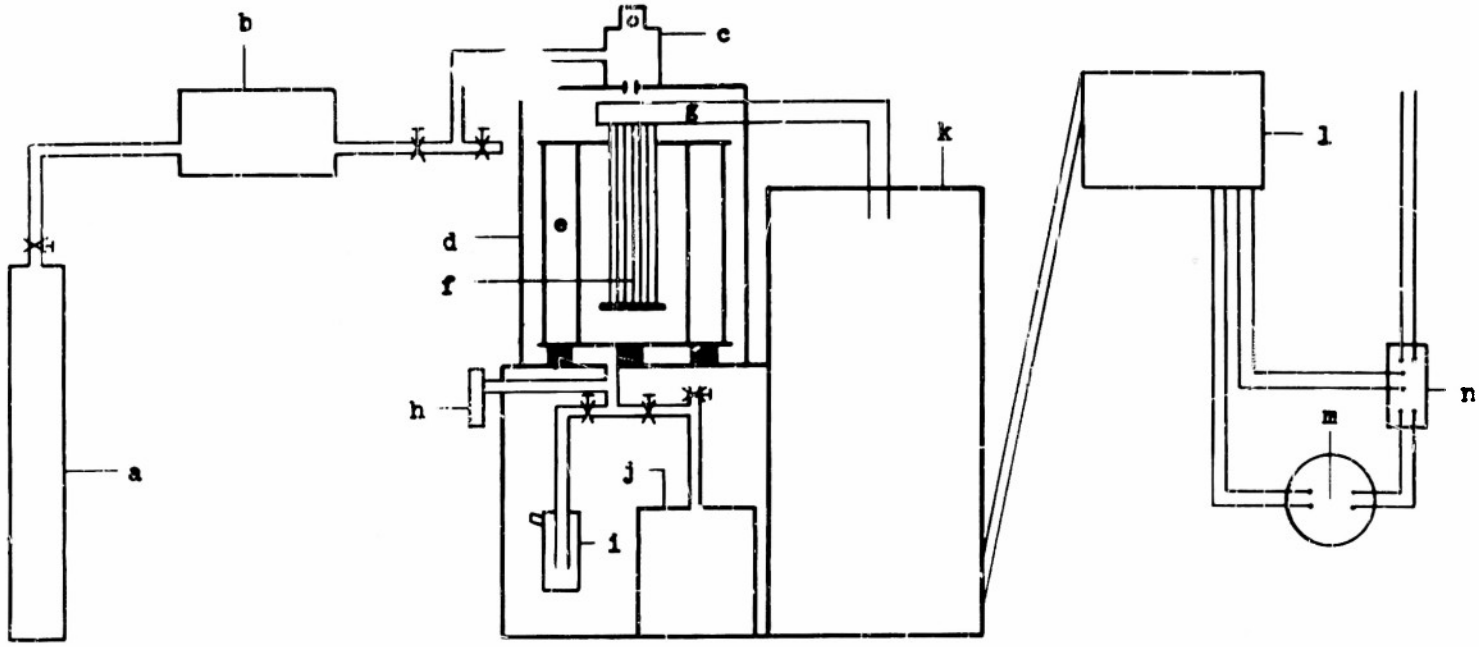


Figure 2a. - Schematic Diagram of Tungsten Grid Resistance Furnace and Auxiliary Equipment

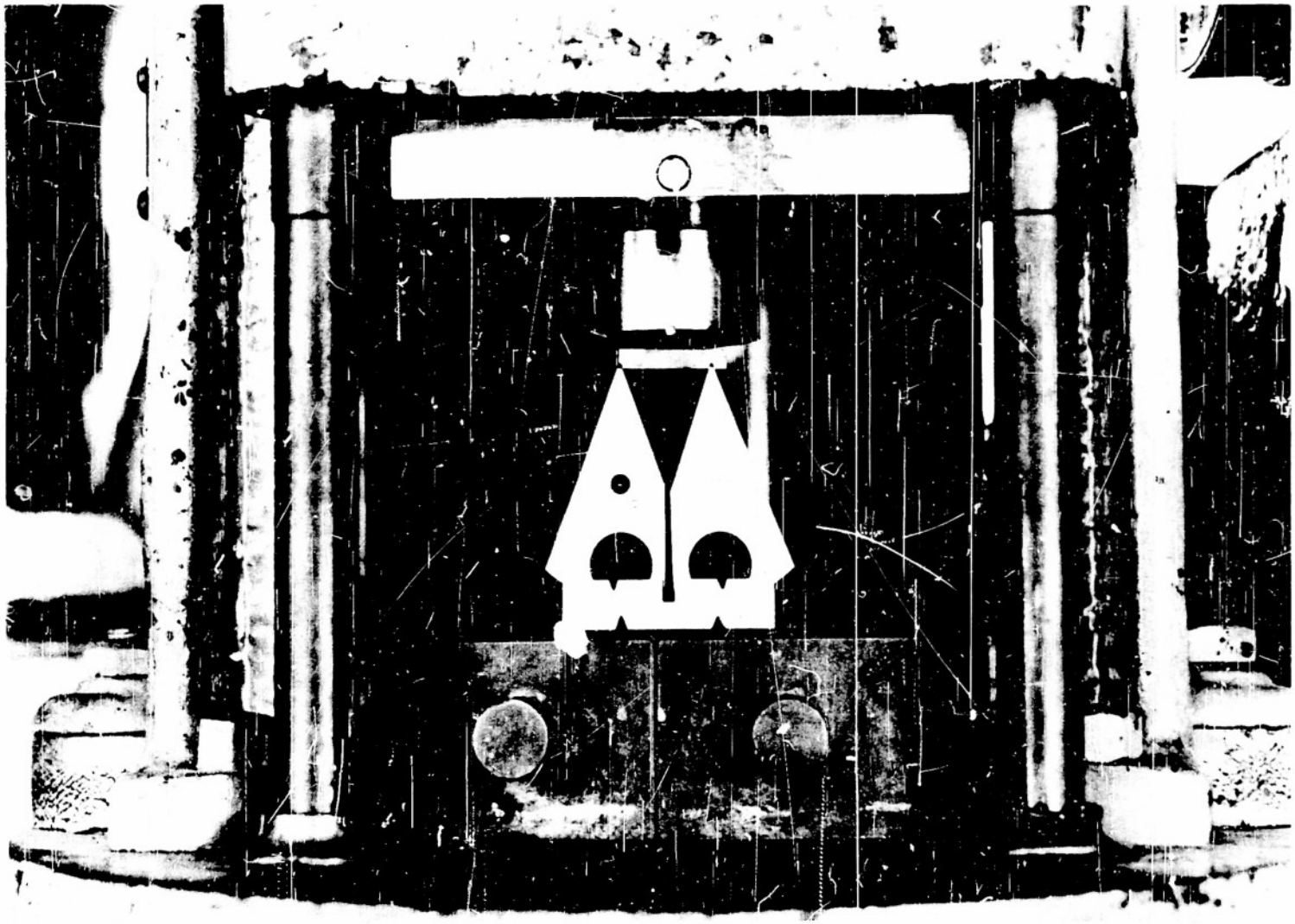


Figure 3. - Original Modulus of Rupture Test Apparatus

Figure 4. - Simplified Modulus of Rupture Test Apparatus

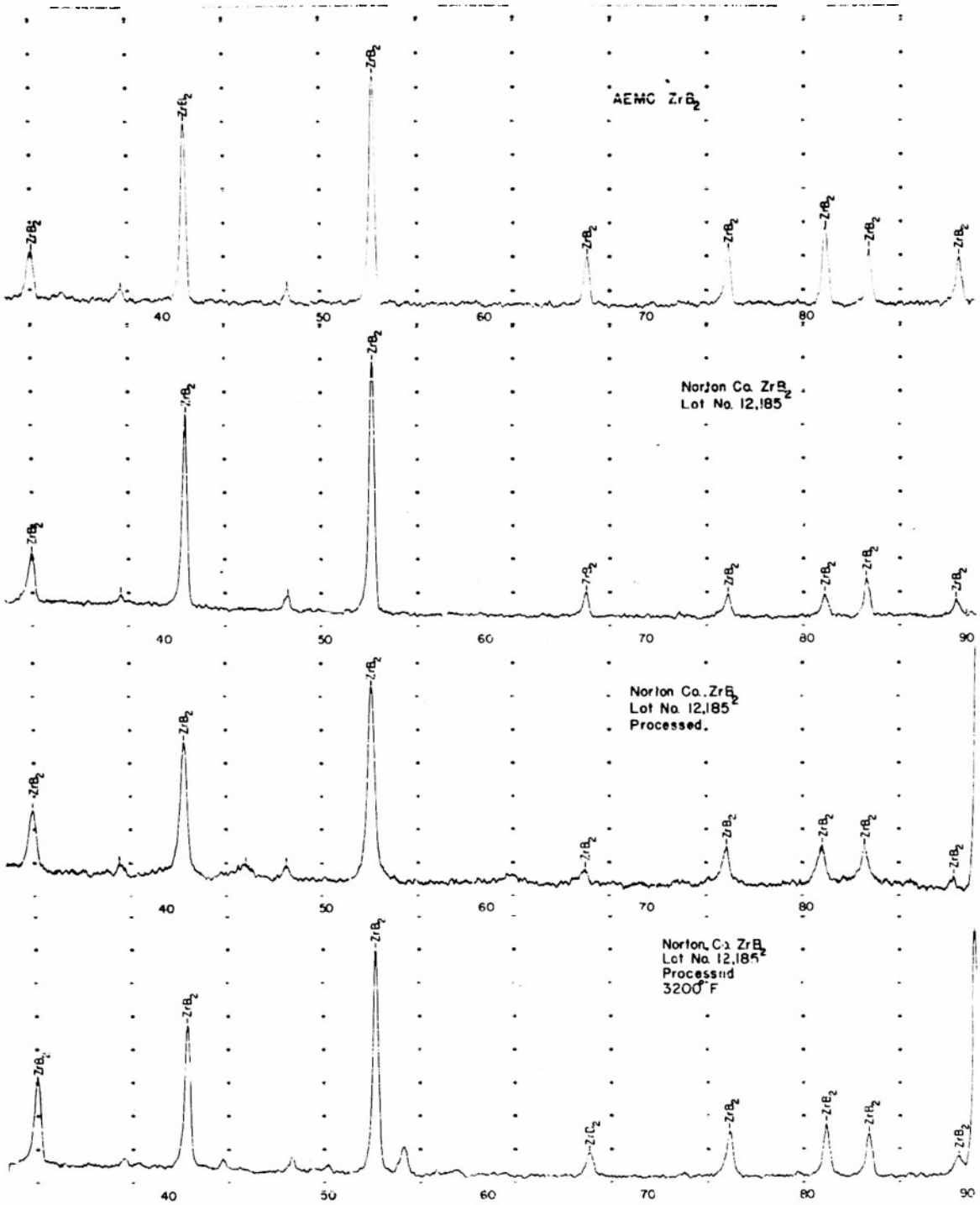


Figure 5. - X-ray Diffraction Patterns of Zirconium Diboride

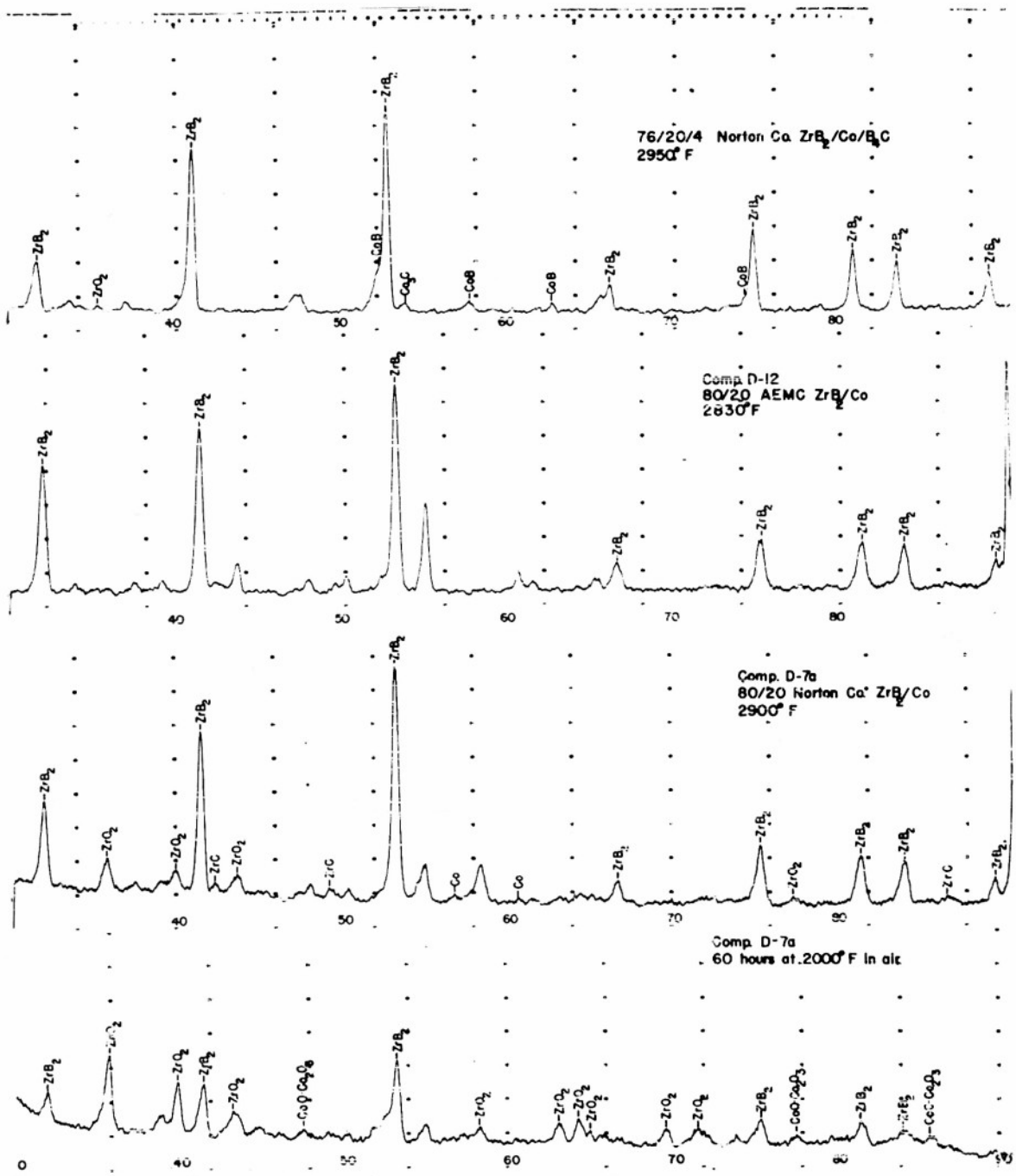


Figure 6. - X-ray Diffraction Patterns of Zirconium Diboride - Cobalt Bodies

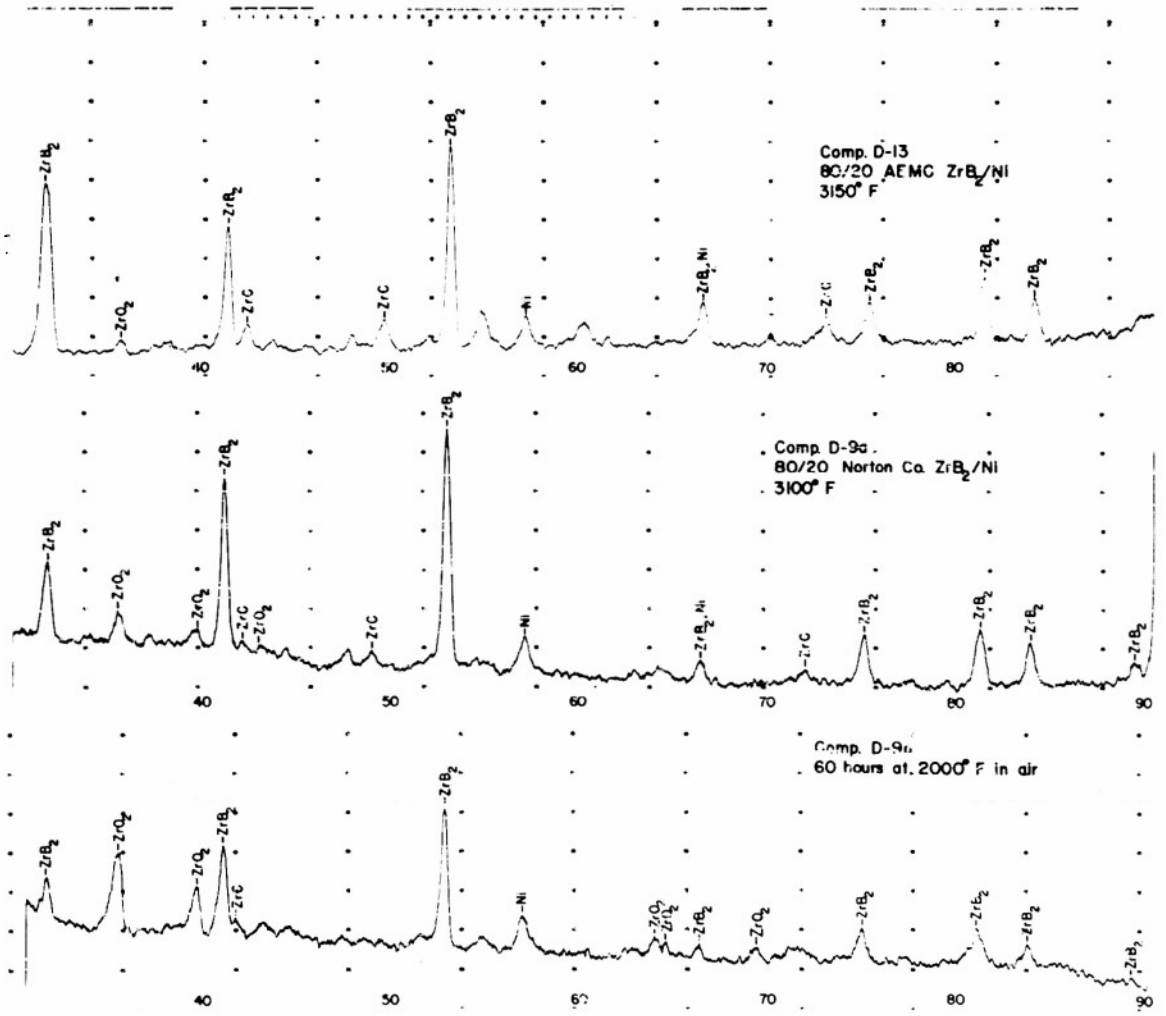


Figure 7. - X-ray Diffraction Patterns of Zirconium Diboride - Nickel Bodies

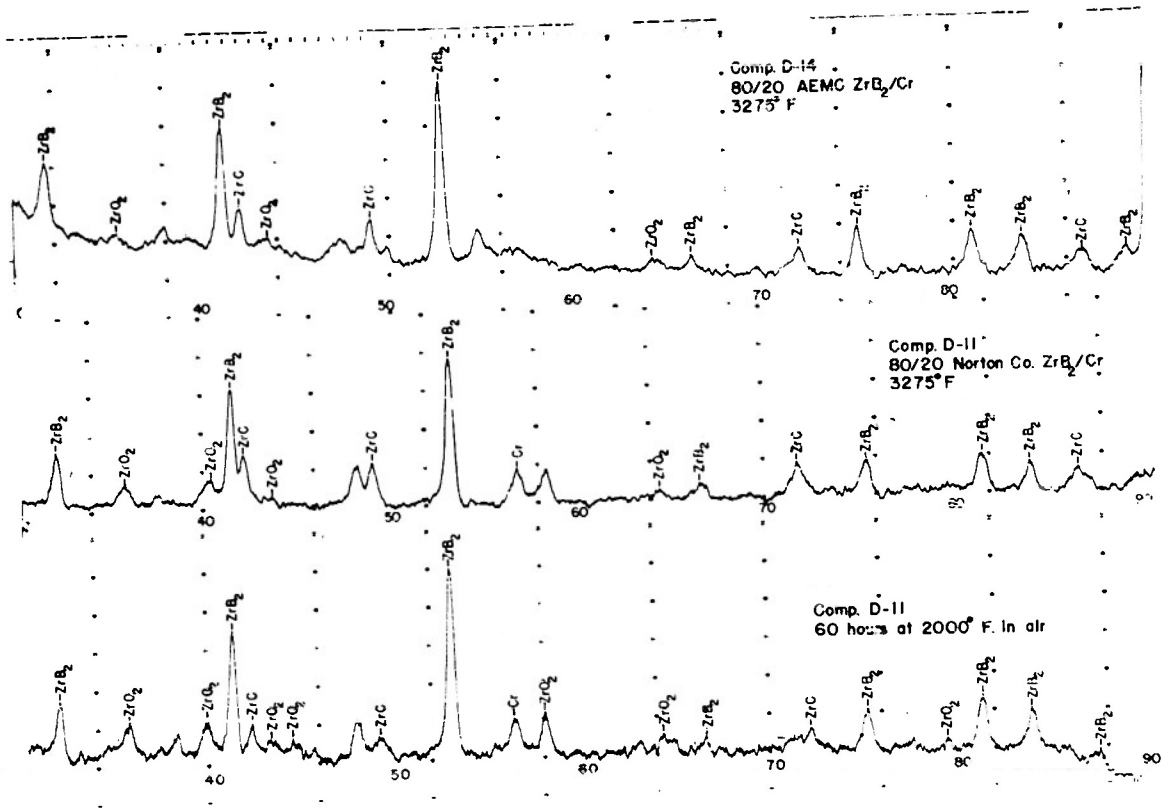


Figure 8. - X-ray Diffraction Patterns of Zirconium Diboride - Chromium Bodies

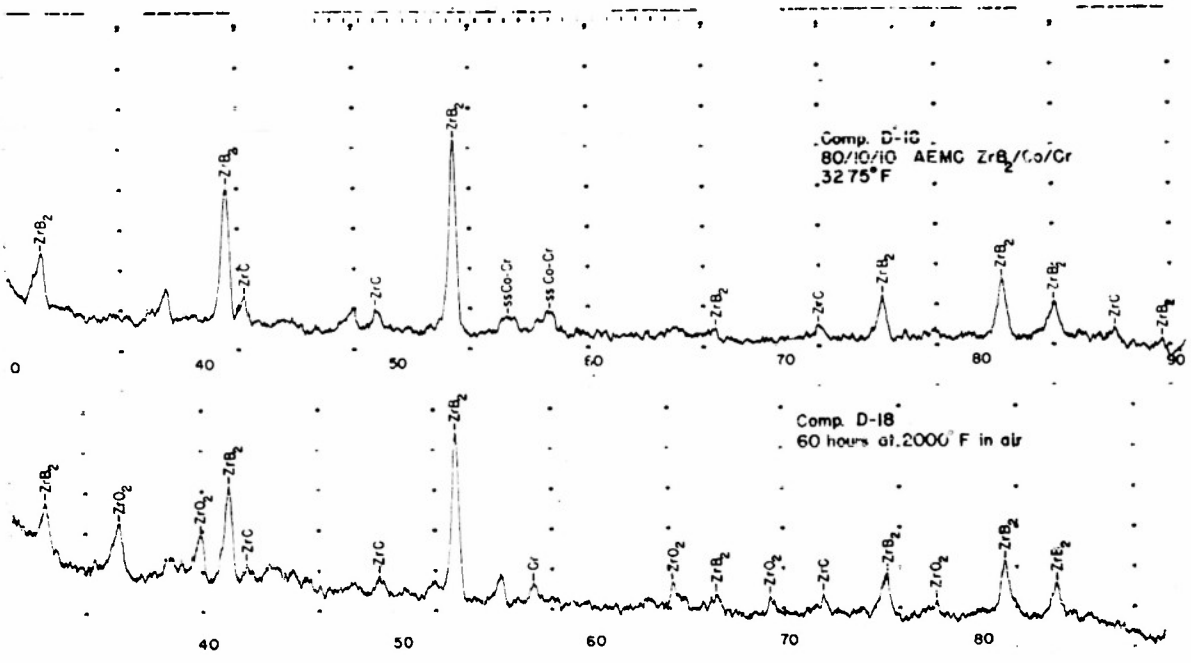
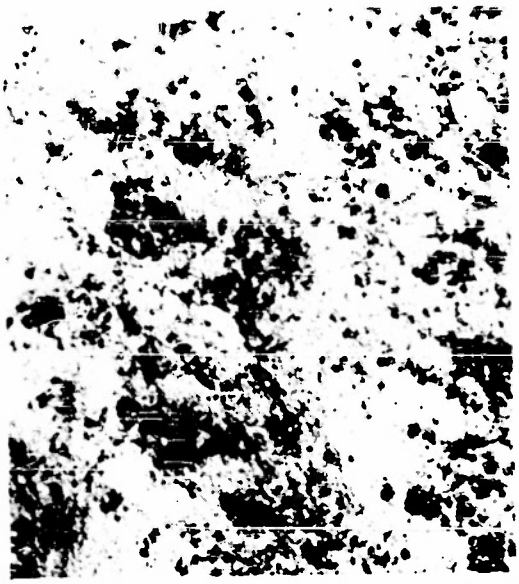


Figure 9. - X-ray Diffraction Patterns of Zirconium Diboride - Cobalt - Chromium Bodies



Body D-7a Density 6.54g/cc
2900°F
20% Co-80% Norton Co. ZrB_2

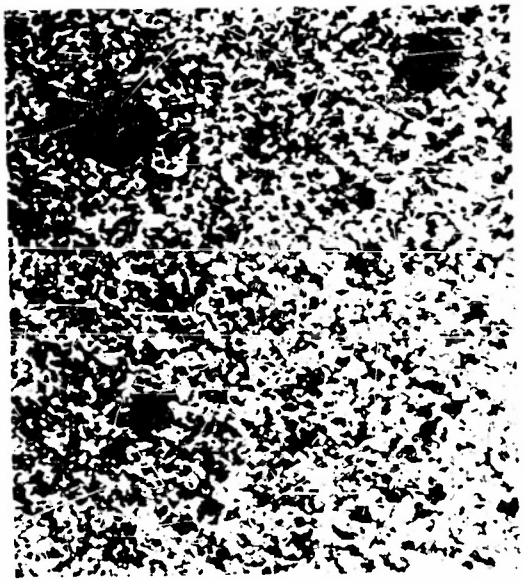
Fig. 10

Body D-9a Density 6.05g/cc
3100°F
20% Ni-80% Norton Co. ZrB_2

Fig. 11

Body D-11 Density 6.40g/cc
3275°F
20% Cr-80% Norton Co. ZrB_2

Fig. 12



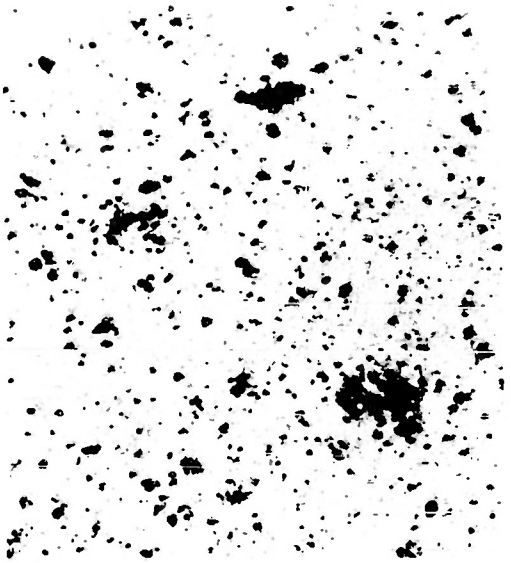
Body D-12 Density 5.48g/cc
2900°F
20% Co-80% AEMC ZrB_2

Fig. 13

Photomicrographs showing the porosity of the fired specimens 100X

Body D-13 Density 5.71g/cc
3100°F
20% Ni-80% AEMC ZrB_2

Fig. 14

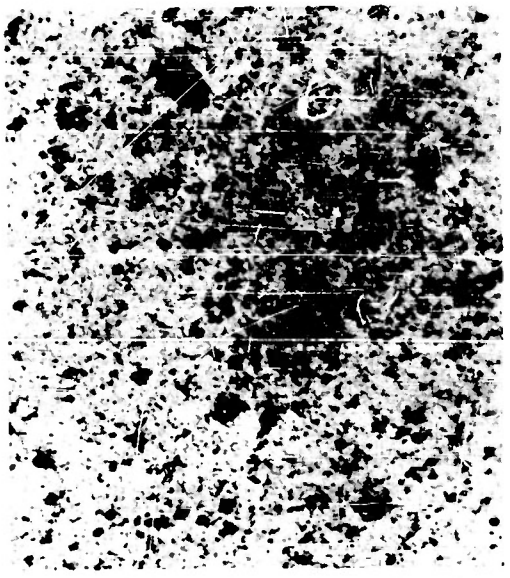


Body D-14 Density 6.38g/cc
3275°F
20% Cr-80% AEMC ZrB_2

Fig. 15

Body D-17 Density 5.63g/cc
3060°F
15% Co-85% AEMC ZrB_2

Fig. 16

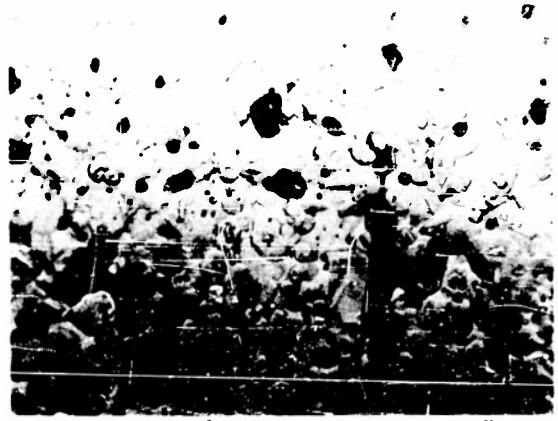


Body D-18 Density 5.95g/cc
3275°F
10% Co-10% Cr-80% AEMC ZrB_2

Fig. 17

Photomicrographs showing the porosity of the fired specimens. 100X

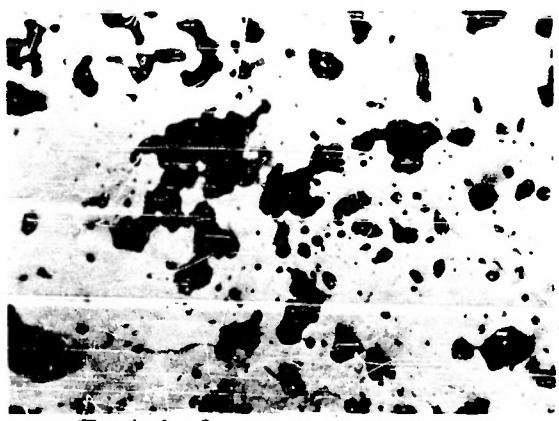
a. Unetched



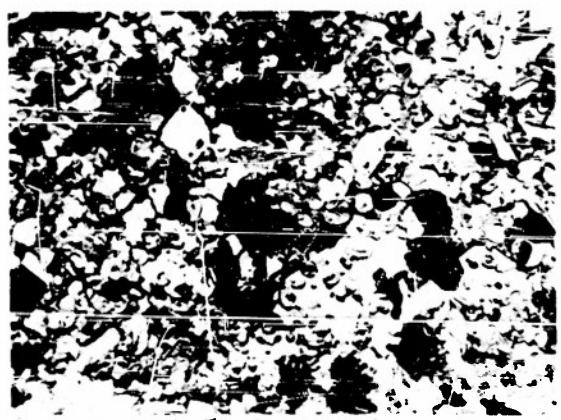
b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

Rounded grains are ZrB_2 which show considerable grain growth. The light areas around the grains are cobalt. The black areas are a glassy material.

Fig. 18 Photomicrograph of polished section of body D-7a - 20% cobalt, 80% Norton Co. ZrB_2 fired at 2900°F in argon. 1000X



a. Unetched



b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

Light grey grains are ZrB_2 which show slight grain growth. The dark grey grains are ZrC. The black areas are a glassy material.

Fig. 19 Photomicrograph of polished section of body D-9a - 20% nickel, 80% Norton Co. ZrB_2 - fired at 3100°F in argon. 1000X

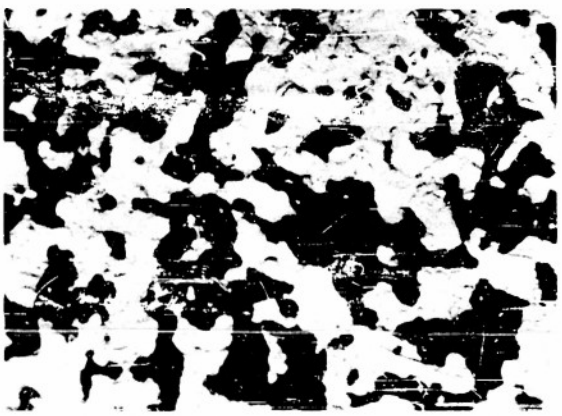
a. Unetched

b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

The whitish grains are ZrB_2 which shows considerable grain growth. The background material is chromium. The grey grains are ZrC. The black areas are a glassy material.

Fig. 20 Photomicrograph of polished section of body D-11 - 20% chromium, 80% Norton Co. ZrB_2 - fired at 3275°F in argon. 1000X

a. Unetched



b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

Light area is ZrB_2 in a matrix of cobalt. Black areas are a glassy phase.

Fig. 21 Photomicrograph of polished section of body D-12 - 20% cobalt, 80% AEMC ZrB_2 fired at 2900°F in argon. 1000X

a. Unetched

b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

The light colored grains are ZrB_2 in a matrix of nickel. The grey grains are ZrC. The black areas are a glassy phase.

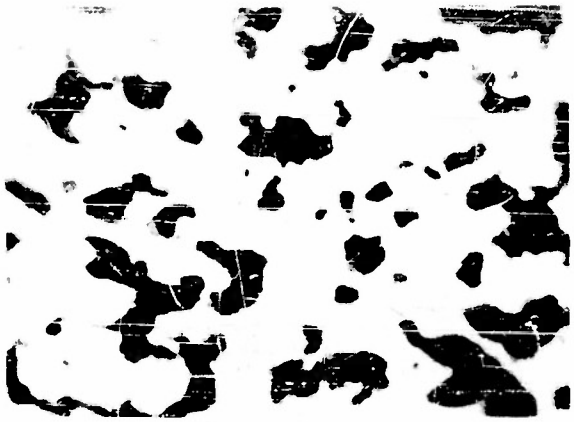
Fig. 22 Photomicrograph of polished section of body D-13 - 20% nickel, 80% AEMC ZrB_2 fired at 3100°F in argon. 1000X

a. Unetched

b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

Light colored grains are ZrB_2 in a matrix of chromium. The grey grains are ZrC. The black areas are a glassy phase.

Fig. 23 Photomicrograph of polished section of body D-14 - 20% chromium 80% AEMC ZrB_2 fired at 3275°F in argon. 1000X

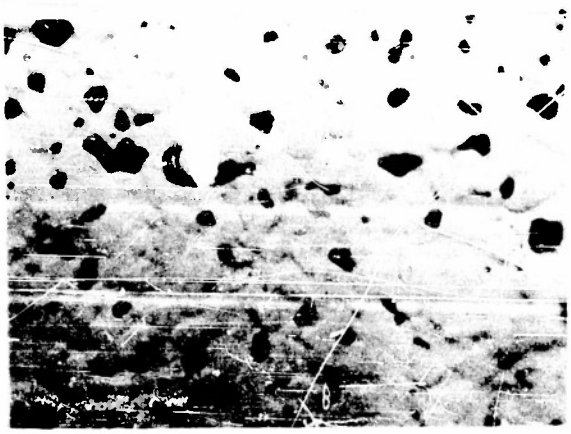


a. Unetched

b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

Light colored grains are ZrB_2 in a matrix of cobalt. Black areas are a glassy phase. The grey grains are ZrC.

Fig. 24 Photomicrograph of polished section of body D-17 - 15% cobalt, 85% AEMC ZrB_2 fired at 3060°F in argon. 1000X

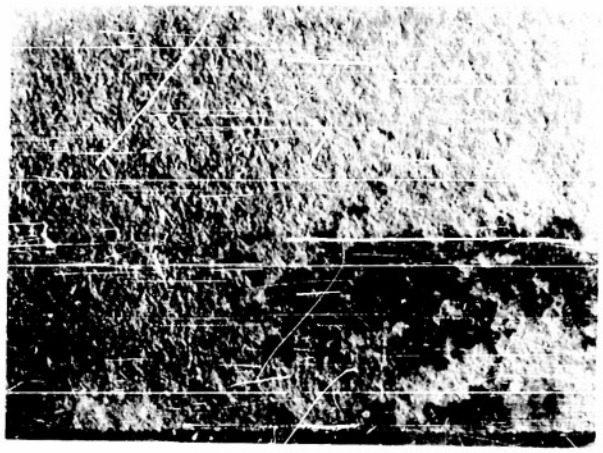


a. Unetched

b. Etched 5 minutes in a solution of 4 parts 48% HF, 2 parts conc. HNO_3 plus 94 parts methanol.

Light colored grains are ZrB_2 which shows appreciable growth and coalescense. The matrix material is an alloy of cobalt and chromium. The grey grains are ZrC. The black areas are a glassy phase.

Fig. 25 Photomicrograph of polished section of body D-18 - 10% cobalt, 10% chromium, 80% AEMC ZrB_2 fired at 3275°F in argon. 1000X



a. Surface of the specimen fired in argon at 2900°F. Dark area is the result of diamond grinding.

7X

b. Surface of bar (a) after 5 hrs. at 2000°F in air. Shows large areas of glass formation. White powdery material is ZrO_2.

7X

c. Section through bar (a) after 60 hours at 2000°F in air. Shows unoxidized material in the oxidized layer.

70X

Figure 26 Photomicrographs of Body D-7a - 80% Norton Co. ZrB_2 plus 20% Co - showing the effects of oxidation at 2000°F.

a. Surface of the specimen fired in argon at 3275°F.

7X

b. Surface of the test specimen (a) after 60 hours at 2000°F in air.

7X

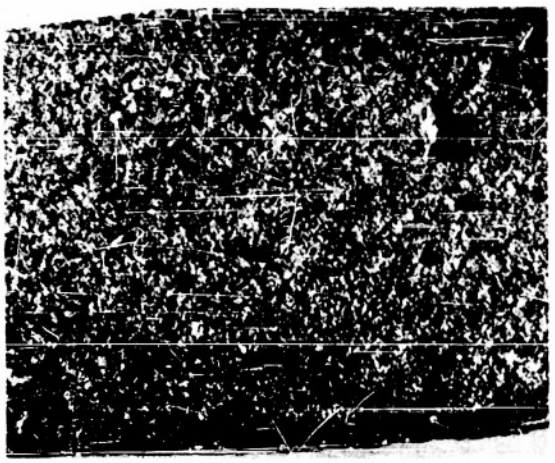
c. Section through the test specimen (b) showing the oxidized layer, zone of reaction and the main body.

70X

Figure 27 Photomicrographs of body D-11 - 80% Norton Co. ZrB_2 plus 20% Cr showing the effects of oxidation at 2000°F.

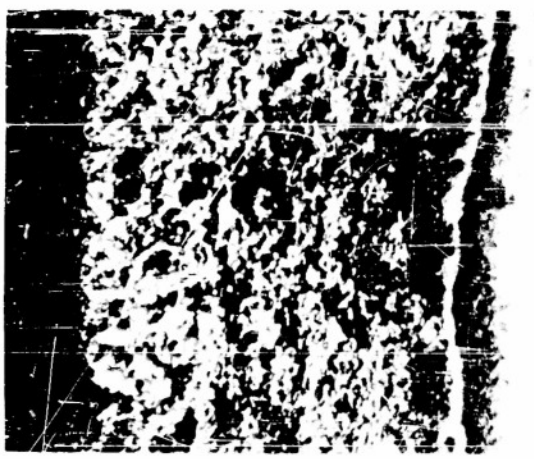
a. Surface of the specimen fired in argon at 3275°F.

7X



b. Surface of the test specimen (a) after 60 hours at 2000°F in air.

7X



c. Section through the test specimen (b) showing the zone of oxidation and the extensive oxide layer.

70X

Figure 28 Photomicrographs of body D-18 - 80% AEMC ZrB_2, 10% Co plus 10% Cr showing the effects of oxidation at 2000°F.

Table I. - Properties of Constituents of Metal Bonded Zirconium Diboride Bodies

Material	Supplier	Purity %	Particle size as received
ZrB_2(1)	Norton Co.	96(2)	40 microns and finer
ZrB_2	American Electro Metals	99	2-4 microns average
Ni	A. D. Mackay	99	9-14 microns
Co	A. D. Mackay	99	300 mesh
Cr	A. D. Mackay	99	40 microns and finer

(1) Lot No. D-12, 185

Zr - 78.44%

B - 18.74

C - 0.46

Fe - 0.42

(2) Estimated from chemical analysis. This material contains boron in excess of that required for the Zr present.

Table II. - Experimental Metal Bonded Zirconium Diboride Compositions

---Per Cent by Weight---

Body No.	Norton Co. ZrB_2	AREMC ZrB_2	Zr	Co	Cr	Ni	Condition of the ZrB_2 as used	Method of mixing batch
D-1	80	--	-	20	--	--	Milled 50 hr.	By hand in agate mortar
D-2	70	--	-	30	--	--	do.	do.
D-3	76	--	4	20	--	--	do.	do.
D-5	72	--	8	20	--	--	do.	do.
D-7	80	--	-	20	--	--	Milled 50 hr. acid leached	do.
D-7a	80	--	-	20	--	--	do.	20 hr. in mill
D-7b	76	--	4*	20	--	--	do.	By hand in agate mortar
D-12	--	80	-	20	--	--	As received	20 hr. in mill
D-16	--	75	-	25	--	--	do.	do.
D-17	--	85	-	15	--	--	do.	do.
D-18	--	80	-	10	10	--	do.	do.
D-11	80	--	-	--	20	--	Milled 50 hr., acid leached	do.
D-14	--	80	-	--	20	--	As received	do.
D-9a	80	--	-	--	--	20	Milled 50 hr., acid leached	do.
D-13	--	80	-	--	--	20	As received	do.

*As ZrB_2

Table III. - Physical Properties of Metal Bonded Zirconium Diboride Compositions

Body No.	Kind & amount metal added	ZrB_2* Used	Type of specimen	Firing temp., °F	Linear fir. shrink, %	Bulk den. g/cc	Modulus of rupture No. bars	Modulus of rupture Psi	Remarks
D-1	Co-20%	N	Cyl.	3200	10.1	6.00	--	------	Hard, strong specimen
D-3	Co-20% Zr-4%	N	Cyl.	3200	----	5.82	--	------	Poor structure
D-5	Co-20% Zr-8%	N	Cyl.	3200	----	5.58	--	------	Very poor structure
D-7	Co-20%	N	Cyl.	3200	11.3	6.00	--	------	Slightly better than D-1
D-7a	Co-20%	N	Cyl.	2900	16.0	6.54	--	------	Cylinder much
		N	Bars	2960	----	6.37	6	21,000	better than D-7.
D-7b	Co-20% Zr-4%**	N	Cyl.	2900	----	----	--	------	Poor structure
D-12	Co-20%	A	Bars	2900	----	5.49	2	8,850	Note lower
			Bars	2850	----	5.48	7	9,030	strength and density as compared to D-7a.
D-16	Co-25%	A	Bars	2840	----	----	--	------	Weak & porous. Bonding metal last to support during firing.
D-17	Co-15%	A	Bars	3060	----	5.63	8	12,570	
D-18	Co-10% Cr-10%	A	Bars	3275	----	5.95	5	11,750	
D-11	Cr-20%	N	Bars	3275	----	6.43	10	21,880	
D-14	Cr-20%	A	Bars	3275	----	6.38	3	34,300	
D-9a	Ni-20%	N	Cyl.	3100	16.0	6.05	--	------	
			Bars	3070	----	6.24	5	22,700	
D-13	Ni-20%	A	Cyl.	3150	10.8	5.71	--	------	
			Bars	3100	----	5.71	4	17,100	

*N-Norton Co. A-American Electro Metals **As ZrH_2